CLAIMS

What is claimed is:

1. A perfluoropolyether comprising perfluoroalkyl radical end groups wherein said radical has at least 3 carbon atoms per radical and is substantially free of perfluoromethyl and perfluoroethyl, and a 1,2-bis(perfluoromethyl)ethylene diradical, $-CF(CF_3)CF(CF_3)-$, is absent in the molecule of said perfluoropolyether.

2. A perfluoropolyether according to claim 1 wherein said perfluoroalkyl radical has 3 to 6 carbon atoms per radical.

3. A perfluoropolyether according to claim 1 wherein said perfluoropolyether has the formula of $C_rF_{(2r+1)}$-A-$C_rF_{(2r+1)}$; each r is independently 3 to 6; if r = 3, both end groups $C_rF_{(2r+1)}$ must be a propyl radical; A is selected from the group consisting of $O-(CF(CF_3)CF_2-O)_w$, $O-(C_2F_4-O)_w$, $O-(C_2F_4-O)_x(C_3F_6-O)_y$, $O-(CF_2CF_2CF_2-O)_w$, $O-(CF(CF_3)CF_2-O)_x(CF_2CF_2-O)_y-(CF_2-O)_z$, and combinations of two or more thereof; w is 4 to 100; and x, y, and z are each independently 1 to 100.

4. A composition comprising a perfluoropolyether, which comprises perfluoroalkyl radical end groups wherein said radical has at least 3 carbon atoms per radical and is substantially free of perfluoromethyl and perfluoroethyl, and 1,2-bis(perfluoromethyl)ethylene diradical, $-CF(CF_3)CF(CF_3)-$, is absent in the molecule of said perfluoropolyether.

5. A composition according to claim 4 wherein said perfluoroalkyl radical has 3 to 6 carbon atoms per radical.

6. A composition according to claim 4 wherein said perfluoropolyether has the formula of $C_rF_{(2r+1)}$-A-$C_rF_{(2r+1)}$; each r is independently 3 to 6; if r = 3, both end groups $C_rF_{(2r+1)}$ must be a propyl radical; A is selected from the group consisting of $O-(CF(CF_3)CF_2-O)_w$, $O-(C_2F_4-O)_w$, $O-(C_2F_4-O)_x(C_3F_6-O)_y$, $O-(CF_2CF_2CF_2-O)_w$, $O-(CF(CF_3)CF_2-O)_x(CF_2CF_2-O)_y-(CF_2-O)_z$, and combinations of two or more thereof; w is 4 to 100; and x, y, and z are each independently 1 to 100.

7. A composition according to claim 4 further comprising a thickener and said perfluoropolyether is present in said composition in the range of from about 0.1 to about 50 weight % based on said composition.

8. A composition according to claim 5 further comprising a thickener and said perfluoropolyether is present in said composition in the range of from about 0.1 to about 50 weight % based on said composition.

9. A composition according to claim 6 further comprising a thickener and said perfluoropolyether is present in said composition in the range of from about 0.1 to about 50 weight % based on said composition.

10. A composition according to claim 9 wherein said thickener is selected from the group consisting of poly(tetrafluoroethylene), fumed silica, and boron nitride, and combinations of two or more thereof.

11. A process for producing a perfluoropolyether comprising (1) contacting a reactant with a metal halide to produce an alkoxide wherein said reactant is selected from the group consisting of a perfluoro acid halide, a C_2 to C_4-substituted ethyl epoxide, a C_{3+} fluoroketone, and combinations or two or more thereof; (2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid halide; (3) esterifying said second acid halide to an ester; (4) reducing said ester to its corresponding alcohol; (5) converting said corresponding alcohol with a base to a salt; (6) contacting said salt with a C_{3+} olefin or perfluoroalkene to produce a fluoropolyether; and (7) fluorinating said fluoropolyether.

12. A process according to claim 11 wherein said C_{3+} olefin is a C_3-C_6 straight chain olefin, C_3-C_6 branched chain olefin, C_3-C_6 allyl halide, or combinations of two or more thereof.

13. A process according to claim 11 wherein said process comprises (1) contacting a perfluoro acid halide or a C_2 to C_4-substituted ethyl epoxide with a metal halide to produce an alkoxide; (2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid halide; (3) esterifying said second acid halide to an ester; (4) reducing said ester to an alcohol; (5) contacting said alcohol with a base to produce a salt; (6) contacting

said salt with a C_3 or higher olefin to produce a fluoropolyether; and (7) fluorinating said fluoropolyether.

14. A process according to claim 11 wherein said process comprises (1) contacting a perfluoro acid halide or a C_2 to C_4-substituted ethyl epoxide with a metal halide to produce an alkoxide; (2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid halide; (3) esterifying said second acid halide to an ester; (4) reducing said ester to an alcohol; (5) contacting said alcohol with a base to produce a salt; (6) contacting said salt with a C_{3+} branched fluoroalkene or a C_{3+} allyl halide to produce a fluoropolyether; and (7) fluorinating said fluoropolyether.

15. A process according to claim 11 wherein said process comprises (1) contacting a perfluoro acid halide or a C_2 to C_4-substituted ethyl epoxide with a metal halide to produce an alkoxide; (2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid halide; (3) esterifying said second acid halide to an ester; (4) contacting said ester with a Grignard reagent to produce a carbinol; and (5) dehydrating or fluorinating said carbinol.

16. A process according to claim 11 wherein said process comprises (1) contacting a C_3 to C_6 fluoroketone with a metal halide to produce an alkoxide; (2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid halide; (3) esterifying said second acid halide to an ester; (4) contacting said ester with a Grignard reagent to produce a carbinol; and (5) dehydrating or fluorinating said carbinol.

17. A process according to claim 11 wherein said process comprises (1) contacting a C_3 to C_6 fluoroketone with a metal halide to produce an alkoxide; (2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid halide; (3) esterifying said second acid halide to an ester; (4) reducing said ester to an alcohol; (5) contacting said alcohol with a base to produce a salt; (6) contacting said salt with a C_{3+} olefin to produce a fluoropolyether; and (7) fluorinating said fluoropolyether.

18. A process according to claim 11 wherein said process comprises (1) contacting a C_3 to C_6 fluoroketone with a metal halide to produce an alkoxide; (2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid halide; (3) esterifying said second acid halide to an ester; (4) reducing said ester to its corresponding alcohol; (5) converting said corresponding alcohol with a base to a salt; (6) contacting said salt with a C_{3+} fluoroalkene to produce a fluoropolyether; and (7) fluorinating said fluoropolyether.

19. A process according to claim 11 wherein said process comprises (1) contacting a perfluoro acid halide or a C_2 to C_4-substituted ethyl epoxide with a metal halide to produce an alkoxide; (2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid halide; (3) contacting said second acid halide with a metal iodide to produce a second iodide; (4) fluorinating said second iodide.

20. A process according to claim 11 wherein said process comprises (1) contacting a C_3 to C_6 fluoroketone with a metal halide to produce an alkoxide; (2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane to produce an acid halide; (3) contacting said acid halide with a metal iodide to produce a second iodide; (4) fluorinating said second iodide.

21. A process according to claim 11 wherein said process comprises (1) contacting a perfluoro acid halide or a C_2 to C_4-substituted ethyl epoxide with a metal halide to produce an alkoxide; (2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid halide; (3) contacting said second acid halide with a metal iodide to produce a second iodide; (4) contacting said second iodide with an olefin to produce a third iodide; and (5) fluorinating said third iodide.

22. A process according to claim 11 wherein said process comprises (1) contacting a C_3 to C_6 fluoroketone with a metal halide to produce an alkoxide; (2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane to produce an acid halide; (3) contacting said acid halide with a metal iodide to produce a second iodide; (4) contacting said second iodide with an olefin to produce a third iodide; and (5) fluorinating said third iodide.

23. A process according to claim 11 wherein said process comprises (1) contacting a perfluoro acid halide or a C_2 to C_4-substituted ethyl epoxide with a metal halide to produce an alkoxide; (2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid halide; (3) contacting said second acid halide with a metal iodide to produce a second iodide; (4) contacting said second iodide with an olefin to produce a third iodide; (5) dehydrohalogenating said third iodide to give a second olefin; and (6) fluorinating said second olefin.

24. A process according to claim 11 wherein said process comprises (1) contacting a C_3 to C_6 fluoroketone with a metal halide to produce an alkoxide; (2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane to produce an acid halide; (3) contacting said acid halide with a metal iodide to produce a second iodide; (4) contacting said second iodide with an olefin to produce a third iodide; (5) dehydrohalogenating said third iodide to give a second olefin; and (6) fluorinating said second olefin.

25. A process according to claim 11 wherein said process comprises fluorinating a fluoropolyether having alkyl radical end groups; said radical has at least 3 carbon atoms per radical and is substantially free of methyl and ethyl; and a 1,2-bis(methyl)ethylene diradical, $-CH(CH_3)CH(CH_3)-$, is absent in the molecule of said fluoropolyether .

26. A process according to claim 25 wherein said process is carried out in the presence of a mixture comprising an inert solvent and a hydrogen fluoride scavenger.

27. A process according to claim 11 wherein said process comprises (1) contacting a perfluoro acid halide or a C_2 to C_4-substituted ethyl epoxide with a metal halide to produce an alkoxide; (2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid halide; (3) contacting said second acid halide with a metal iodide to produce a second iodide; (4) replacing the iodine radicals of said second iodide with hydrogen radicals to produce a fluoropolyether containing hydrogen radicals; and (5) fluorinating said fluoropolyether.

28. A process according to claim 11 wherein said process comprises (1) contacting a C_3 to C_6 fluoroketone with a metal halide to produce an alkoxide; (2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane to produce an acid halide; (3) contacting said acid halide with a metal iodide to produce a second iodide; (4) replacing the iodine radicals of said second iodide with hydrogen radicals to produce a fluoropolyether containing hydrogen radicals; and (5) fluorinating said fluoropolyether.

29. A process according to claim 11 wherein said process comprises (1) contacting a perfluoro acid halide or a C_2 to C_4-substituted ethyl epoxide with a metal halide to produce an alkoxide; (2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid halide; (3) contacting said second acid halide with a metal iodide to produce a second iodide; (4) contacting said second iodide with an olefin to produce a third iodide; (5) replacing the iodine radicals of said second iodide with hydrogen radicals to produce a fluoropolyether containing hydrogen radicals; and (6) fluorinating said fluoropolyether.

30. A process according to claim 11 wherein said process comprises (1) contacting a C_3 to C_6 fluoroketone with a metal halide to produce an alkoxide; (2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane to produce an acid halide; (3) contacting said acid halide with a metal iodide to produce a second iodide; (4) contacting said second iodide with an olefin to produce a third iodide; (5) replacing the iodine radicals of said second iodide with hydrogen radicals to produce a fluoropolyether containing hydrogen radicals; and (6) fluorinating said fluoropolyether.

31. A process according to claim 11 wherein said process comprises (1) contacting a perfluoro acid halide, a C_3 to C_6 fluororoketone, or a C_2 to C_4-substituted ethyl epoxide with a metal halide to produce an alkoxide; (2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid halide; (3) esterifying said second acid halide to an ester; (4) reducing said ester to an alcohol; (5) contacting said alcohol with sulfur tetrafluoride or derivative thereof to convert the OH groups of said alcohol to

fluorine radicals thereby producing a fluoropolyether; and (6) fluorinating said fluoropolyether.

32. A process according to claim 11 wherein said process comprises (1) contacting a perfluoro acid halide, a C_3 to C_6 fluoroketone, or a C_2 to C_4-substituted ethyl epoxide with a metal halide to produce an alkoxide; (2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid halide; (3) esterifying said second acid halide to an ester; (4) reducing said ester to an alcohol; (5) contacting said alcohol with a phosphorus pentahalide or derivative thereof to convert the OH groups of said alcohol to halide radicals thereby producing a fluoropolyether; and (6) fluorinating said fluoropolyether.

33. A process according to claim 11 wherein said process comprises (1) contacting a fluorotertiary alkoxy-containing compound with a first fluoropolyether to produce a second fluoropolyether and optionally (2) fluorinating said second fluoropolyether wherein said fluorotertiary alkoxy-containing compound is a salt of a fluorotertiary alcohol or a perfluoro-t-butyl hypofluorite; said first fluoropolyether has (i) a starting C_3-C_6 segment or $R_f^8(R_f^9)CFO$ segment and (ii) a -A-O-$C(CF_3)$=CF_2 or a -A-O-$C(CF_3)$=CHF intermediate end group; R_f^8 is $C_jF_{(2j+1)}$; R_f^9 is $C_kF_{(2k+1)}$; j and k are each ≥ 1; $(j + k) \leq 5$; and A is selected from the group consisting of $O\text{-}(CF(CF_3)CF_2\text{-}O)_w$, $O\text{-}(CF_2\text{-}O)_x(CF_2CF_2\text{-}O)_y$, $O\text{-}(C_2F_4\text{-}O)_x$, $O\text{-}(C_2F_4\text{-}O)_x(C_3F_6\text{-}O)_y$, $O\text{-}(CF(CF_3)CF_2\text{-}O)_x(CF_2\text{-}O)_y$, $O(CF_2CF_2CF_2O)_w$, $O\text{-}(CF(CF_3)CF_2\text{-}O)_x(CF_2CF_2\text{-}O)_y\text{-}(CF_2\text{-}O)_z$, and combinations of two or more thereof.

34. A process according to claim 33 wherein said fluorotertiary alkoxy-containing compound is a salt of a fluorotertiary alcohol.

35. A process according to claim 33 wherein said fluorotertiary alkoxy-containing compound is a perfluoro-t-butyl hypofluorite.